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LIQUID CHROMATOGRAPHY APPLICATIONS TO DETERMINA-TION OF SORPTION ON AQUIFER MATERIALS

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Sorption coefficients of 1-methylnaphthalene and 1,2-dichlorobenzene in aqueous solution were measured on six aquifer materials by column chromatography using frontal analysis. Results were compared with sorption coefficients for the same systems determined by the batch method. Column values did not exceed batch values, and were generally near 0.5 times the batch values. The order of sorption coefficients on the aquifer materials was the same for both methods.

Possible reasons for this disagreement and limitations of column methods with aquifer material packing are discussed. It is suggested that column methods of aquifer material packing are discussed. It is suggested that column methods of sorption coefficient determination have several disadvantages and that batch methods should be preferred.

Transport equations in aquifers for sorbates with non-linear isotherms have been developed. A field test of effects of non-linear sorption behavior on sorbate plume shape and extent is proposed.

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PREFACE

This report was originally submitted for publication in <u>Chemosphere</u>. Work documented in the report was performed by Dr W. G. MacIntyre and Dr T. B. Stauffer for the Air Force Engineering and Services Center, Engineering and Services Laboratory, Tyndall Air Force Base, Florida 32403-6001.

This report is being published in the same format as the journal article for the benefit of the reader and because of its interest to the worldwide scientific and technical community.

Dr Thomas B. Stauffer was the AFESC/RDV project officer. Work documented in this report was performed between October 1986 to October 1988.

This report has been reviewed by the public affairs office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

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iii
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INTRODUCTION:

Many workers have applied column chromatography to groundwater contaminant transport problems and several have missed the conclusion of Bear (1979), who states that, "because of both technical and scaling difficulties, the sand box model cannot be used as a tool for solving boundary value problems of practical interest. The column filled with a porous medium, however, is a very important laboratory research tool suited for observing phenomena (also of solute transport with or without solid-liquid interaction) and verifying approximate solutions". Investigations reported here on sorption coefficient measurement of single sorbates and sorbate mixtures on aquifer material columns were done in accordance with this caveat.

In this work, chromatography columns were packed with aquifer material and sorption coefficients were determined by frontal analysis. This chromatographic measurement of equilibrium sorption was developed by James and Phillips (1954) among others, elaborated by Jacobson et al (1984), and applied to soils and aquifer materials by eg. Bilkert and Rao (1985), Schwarzenbach and Westall (1981), Goerlitz (1984), Kay and Elrick (1967), Russell and McDuffie (1986). It has also been used on synthetic sorbates (e.g., Sharma and Fort 1973). Chromatographic measurements of equilibrium sorption are generally referred to as dynamic, in contrast to conventional batch (static) equilibrium sorption measurements. Under ideal conditions, equilibrium sorption isotherms for a given solvent-sorbate-sorbent system should be independent of whether the isotherm is determined by a dynamic or static method. The thermodynamics of sorption from simple solution has been presented by Everett and Podoll (1979), who also consider isotherm

measurements by dynamic and static methods. In the present work, equilibrium sorption data on water-nonionic organic compound-aquifer material systems are determined by both dynamic and static methods. Results are compared and reasons for differences between the methods in this application to aquifer materials are discussed. Conditions for ideal liquid column chromatography with frontal analysis are given by Snyder and Kirkland (1979). Among these are: constant flow velocity, uniformity of packing particle size, homogeneous packing, absence of column wall and end effects, complete retention of packing by a packing retainer, flow velocity low enough to attain local equilibrium of solute between solvent and packing but high enough so dispersion does not override sorption effects. Some of these conditions cannot be met with aquifer material packing, so they must be approached as closely as possible.

Transport of solute through a column is well known for the case of solute sorption with a linear isotherm. The sorbates used here, 1-methylnaphthalene and 1,2-dichlorobenzene have linear isotherms on the aquifer materials selected. The operation of a finite length (L) ideal column is described following Bear (1979) for the case of linear sorption in terms of the one-dimensional mass balance equation.

$$\frac{\partial C}{\partial t} + \frac{u_o}{\dfrac{(1 + k\rho_b)}{\varepsilon}} \frac{\partial C}{\partial Z} = \frac{D}{\dfrac{(1 + k\rho_b}{\varepsilon}} \frac{\partial^2 C}{\partial z^2})$$

where C is the solute concentration in the liquid phase, D is the axial

dispersion coefficient, u_o is the liquid flow velocity, k is the sorption coefficient, Z is distance (axial) and t is time, ρ_b is packing bulk denisty and ϵ is porosity.

For frontal chromatography the initial and boundary conditions are:

at $t < 0$ for $z > 0$, $C = 0$, initial condition;

for $t > 0$ for $z = 0$, $(C_o - C)\, u_o = -D\, \dfrac{\partial C}{\partial z}$, inlet boundary condition;

$z = L$, $\dfrac{\partial C}{\partial z} = 0$, outlet boundary condition.

The inlet boundary condition corrects the concentration gradient for dispersion, while the outlet boundary condition implies flow into a gas continuum. Bastian and Lapidus (1956) have provided an analytic solution for this situation (i.e., a functional relation for $C(Z,t)/C_o$, where C_o is the column feed concentration.

The column output response is affected by dispersion of the solute indicated by the term $\dfrac{D}{\dfrac{(1 + k\rho_b)}{\epsilon}}\, \dfrac{\partial^2 C}{\partial z^2}$ and by advection of the solute

indicated by the term $\dfrac{u_o}{\dfrac{(1 + k\rho_b)}{\epsilon}}\, \dfrac{\partial C}{\partial Z}$. Both terms contain the equilibrium

sorption coefficient. For constant C, u_0, D, and k, the breakthrough curve for C/C_0 versus time at the outlet is sigmoid as shown in Fig. 1. Frontal elution occurs at time t_1 for an unretained solute and t_2 for a retained solute.

The difference in area between the two curves in Fig. 1 is a measure of the retained solute sorption coefficient k. Letting C_1 be the concentration of unretained solute and C_2 be the concentration of the retained solute, with the subscript (0) indicating input concentration, the elution time t_1 equals $\dfrac{1}{C_1(0)} \int_0^\infty C_1 dt$, and the retention volume V_1 equals $u_0 t_1$.

A similar expression determines V_2, the retention volume of the sorbed solute. A point on the isotherm corresponding to sorbate equilibrium concentration C_2 is calculated as given by Jacobson et al (1984), namely,

$$\frac{q_2}{C_{2(0)}} = \frac{V_2 - V}{Vsp}$$

where q_2 = equilibrium concentration of sorbate on sorbent at $C_{2(0)}$, and Vsp is the volume of sorbent in the column. Vsp is usually determined gravimetrically. V_1 is often called the column dead volume. Units used here are $C_{2(0)}$ in mmol and q_2 in mmol/ml of sorbent.

There are several practical difficulties that must be confronted. A complete isotherm by frontal analysis requires repeat column runs at several $C_{2(0)}$ values to establish isotherm points. This is a slow process because u_0 must be low enough to achieve local equilibrium. No retainer could hold
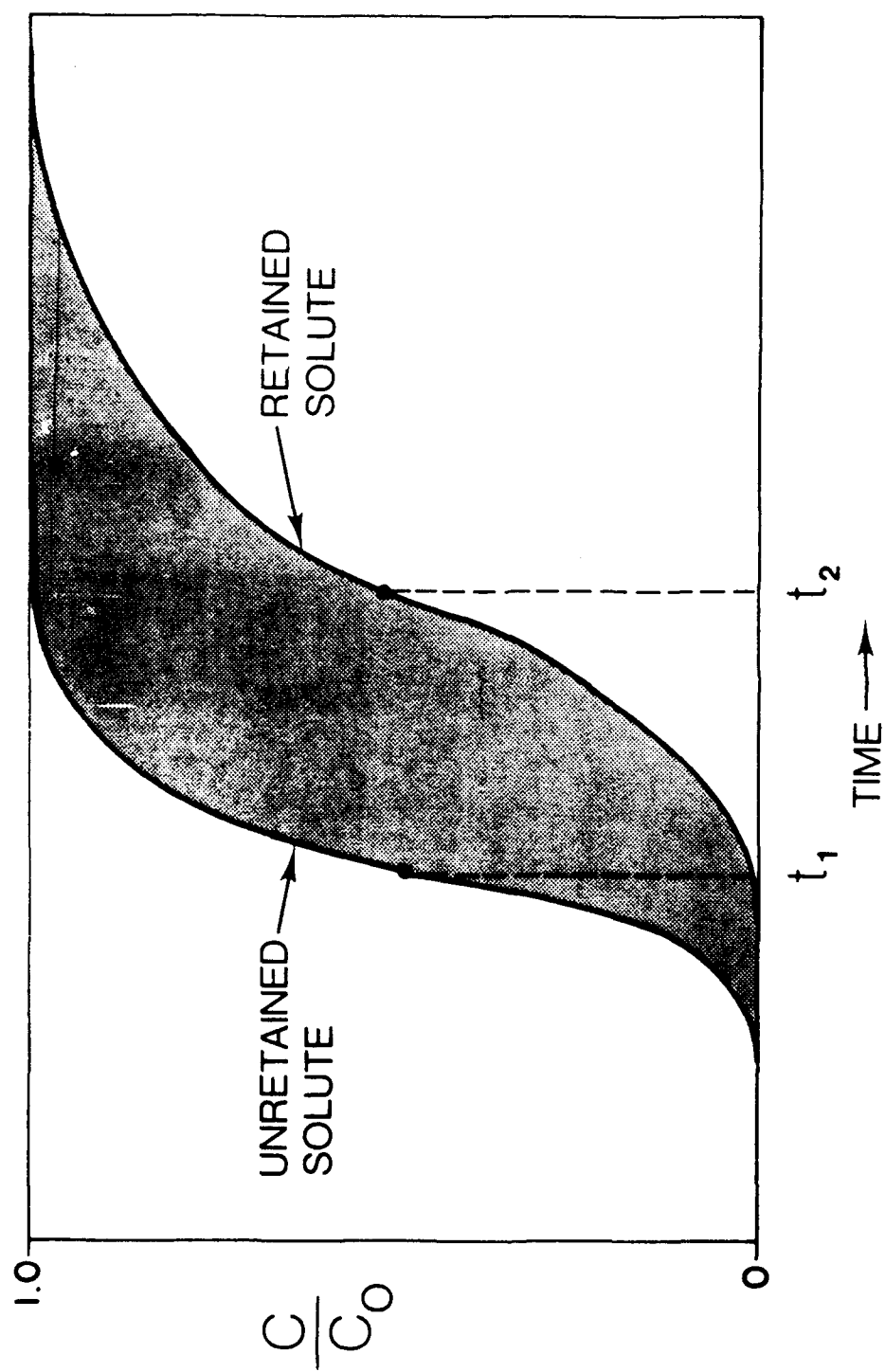
Fig. 1. An example of normalized breakthrough curves for retained and unretained solutes.

up the aquifer fines without acting as a sorbent and producing excessive backpressure at practical flow rates. There is no way to homogeneously pack aquifer materials in a column because of non-uniform particle size. Channeling may occur and not be detected. Plug flow may not occur due to column wall and end effects. Flow may be too fast for local equilibrium attainment. There is no completely unretained solute to measure V_1, so the least unretained solute must be used. Sorption by the chromatographic apparatus may cause error in the calculated sorption coefficient.

Previous researchers using soils and aquifer materials did not state column packing retainer characteristics. Concern developed here when aquifer material fines were noted to pass through the 2 micron stainless steel frits used in trial column loading and flushing tests (and throughout the later experimentation). Goerlitz (1984), Wilson et al (1981), Russell and McDuffie (1986) and Nkedi-Kizza et al (1983) reported experiments on columns packed with soil or aquifer material, but did not adequately specify the retainer material and pore size. There is an apparent lack of concern with particle retention, but the effects of particle losses on sorption coefficients cannot now be estimated. The aquifer materials used here were selected from a number of geological settings and all contained considerable fines. It is assumed that the loss of fines will be a problem in column work with most aquifer materials, and this is now being investigated.

Materials

$CaCl_2 2H_2O$ (Baker Reagent Grade) was used to prepare $CaCl_2$ solutions.

Reagent grade 1-methylnaphthalene ($1CH_3N$) and 1,2 dichlorobenzene (ODCB) of 99 percent purity were used as obtained from the suppliers,

Aldrich Chemical Co., Inc., Milwaukee, WI, and Fluka Chemical Co., Ronkonkoma, NY, respectively. Water was MiliQ (Milipore Corp.) treated after distillation in glass. Solvents used for cleaning apparatus and extraction were Burdick and Jackson distilled-in-glass CH_3Cl, acetone and hexane from American Scientific Products Co. JP-4 jet fuel was supplied by the Defense Logistics Agency Fuel Depot at Lynn Haven, FL.

Aquifer materials were obtained from several sources. Lula material was collected at a depth of 5m from the Johnson Ranch near Lula, OK, and provided by Robert S. Kerr Environmental Research Laboratory (EPA). Ada, OK. The USAF provided aquifer materials from its bases (which are used as the sample names). Tinker material was collected near Oklahoma City, OK, from a depth of 4.9 - 8.7m. Barksdale aquifer material was collected near Shreveport, LA, from a depth of 4.3 - 13.9m. Blytheville aquifer material was collected near Blytheville, AR, from a depth of 8.8 - 10.0m. Carswell material was collected near Fort Worth, TX, from a depth of 1.3 - 6.4m. Canadian Borden site material was a subsample of the bulk sample provided by Mackay et al (1986). Characteristic properties and mineralogical description of these samples are given in detail by Stauffer (1987) and selected values are presented in Table 1.

Table 1. Aquifer Material Properties.

Aquifer Material	TOC (%)	CEC (mcq/100g)	Surface Area (m_2/g)	Sand (%)	Clay (%)	Silt (%)	Iron (%)
Tinker	0.010	20.9	9.2	40.8	4.7	53.1	1.4
Carswell	0.027	8.0	9.5	74.8	NR	18.2	0.9
Barksdale	0.105	32.4	7.5	52.3	NR	41.5	1.0 .
Blytheville	0.156	18.1	8.0	67.8	3.5	27.3	0.7

Borden	0.015	NA	0.3	96.0	2.0	2.0	1.5
Lula	0.020	6.3	11.8	91.0	3.4	5.6	2.9

NA = not analyzed.
NR = not measurable in sieve.

Experimental Methods.

The chromatographic apparatus was constructed of stainless steel and glass to minimize sorption problems, and is shown in Fig. 2. All columns used were 25 cm long stainless steel liquid chromatography blanks with stainless steel packing retainers supplied by Supelco, Bellfonte, PA. Column retainer frits were 2 micron pore size. The switching valve was a low dead volume manual, 6 port, Nitronic-60 alloy Valco unit with 1/16" zero volume fittings supplied by Supelco. All tubing and connections were stainless steel. Tubing ID was 0.010" ID used in minimum lengths. Detectors were an ISCO variable wavelength uv model V4 and a Perkin-Elmer refractive index model LC-25. A Gilson (Middleton, WI) model FC-80N fraction collector was used to collect portions of column effluent for analysis of Cl^- by titration with silver nitrate.

Chromatographic determination of a sorption isotherm point required about 100 hours. Detector signals were recorded on a Hewlett-Packard 3357 laboratory data system. Files of 540 min duration were taken, transferred to the Hewlett-Packard RPN program and merged to make a complete file for a chromatography run Frontal analysis integrations were done on the merged files by commands in the RPN system.

Frontal analysis was done after preparation of a saturated solution of the organic sorbate in water. Saturation vessels and techniques used in sorbate solution preparation are described in Burris and MacIntyre (1985).

Solutions were prepared in 0.015M $CaCl_2$. Experiments were conducted at a laboratory temperature of $22°C \pm 2°C$. The saturated solution was then transferred to a glass mixing chamber by positive pressure as shown in Fig. 3. Dilution water 0.015M in $CaCl_2$ was added to make up the desired solution concentration. The contents of this mixing chamber were transferred immediately to the HPLC pump 2 chamber. Occasional checks of the sorbate concentration were made on 20 mL portions taken from the pump delivery as described by Burris and MacIntyre (1986). Concentrations of sorbates are reported as fractions of their saturation concentration value, and values above 0.75 times saturation concentration were avoided due to potential problems with sorption on the apparatus or nonlinearity in sorbate isotherms. Pump 1 was filled with 0.01M $CaCl_2$. Both pumps were set to the same flow rate and the column was flushed till the solute was free of visible particles and the uv detector output was steady. The valve was then rotated, producing a step increase from 0.01M to 0.015M in CaC_2 concentration and from zero to the specified organic sorbate concentration. This generated fronts for analysis. The $CaCl_2$ breakthrough was detected by refractive index, and later by fraction collection and $AgNO_3$, titration of each fraction. Breakthrough of organics was detected by uv absorbance at 281 nm for 1-methylnaphthalene and 268 nm for 1,2-dichlorobenzene. Confirmation of organic breakthrough was determined by manual collection of samples at regular intervals as shown in Fig. 4. This technique was also used for organic sorbate mixtures because uv spectrophotometric detection was unsuitable for multiple solute effluents. After collection, a known volume of hexane containing an internal standard was injected through the bottle septum cap and a single extraction was done. A portion of the hydrocarbon phase was removed by a syringe needle and injected in a GC for
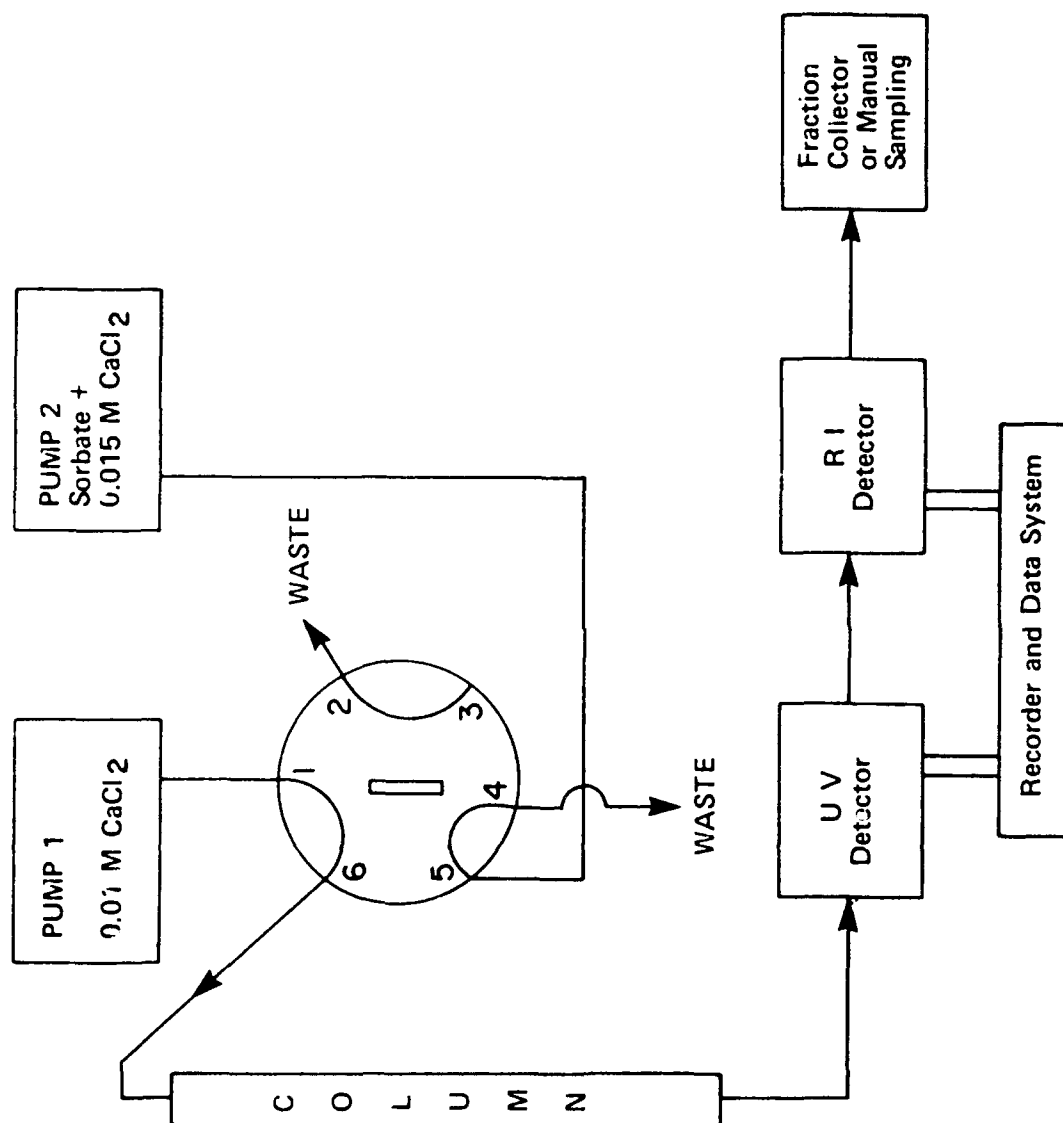
Fig. 2. Schematic of chromatography apparatus.

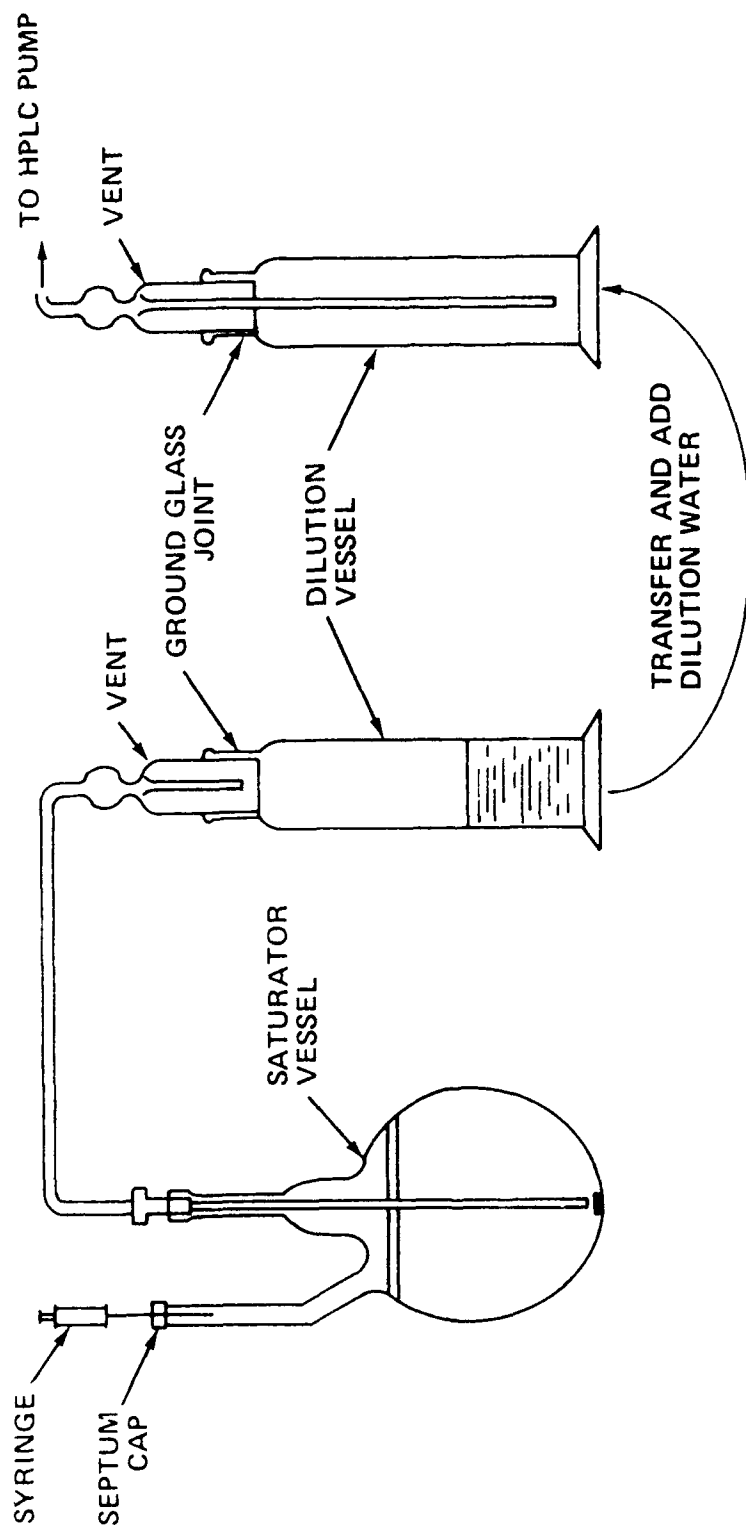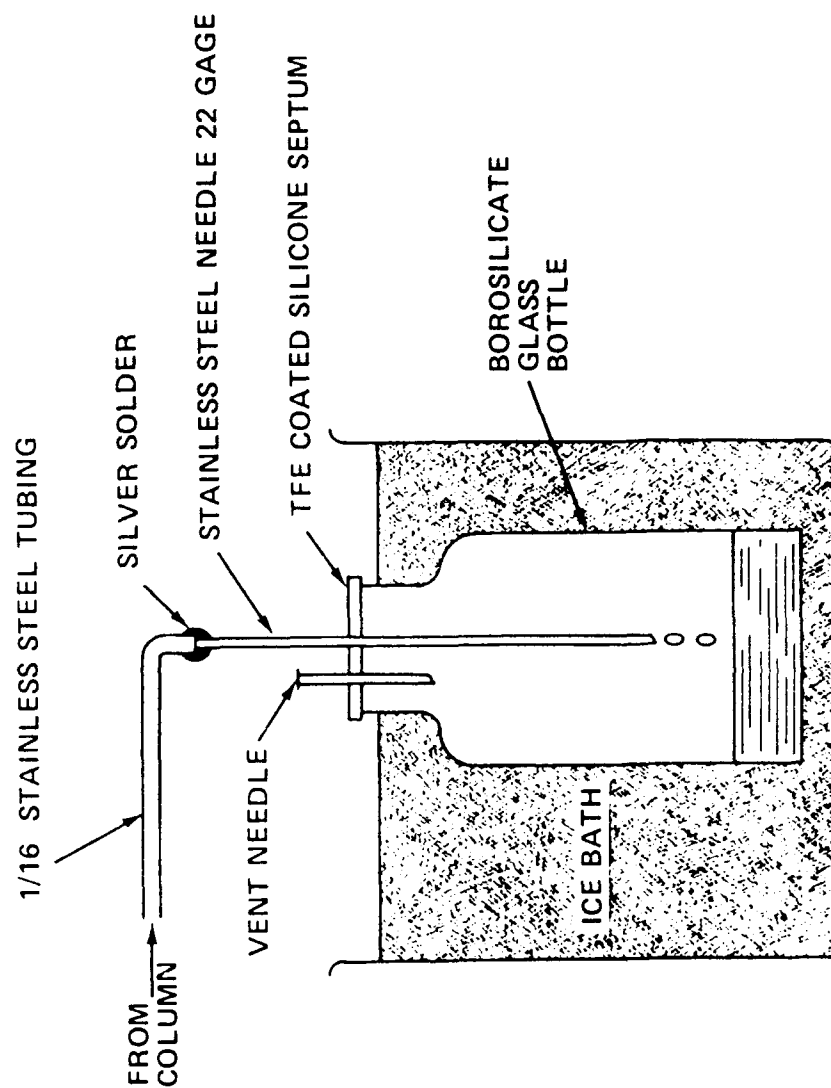Fig. 3. Sorbate solution preparation and transfer to pump.

Fig. 4. Manual collection of column fractions.

analysis. It was later noted that a similar method was used by Patrick et al (1985) in analysis of groundwater samples.

Selection of Flow Velocity.

Dispersion in LC columns causes peak broadening and is avoided in analytical applications by using fast flow rates and small particles with thin layer coatings so local equilibrium is quickly approached. This involves careful design of packing materials. It is impossible to optimize flow conditions for aquifer material column packings, because many different incompletely known particle types and sizes are present. However, some generalizations remain applicable for aquifer material packing. High flow velocities give less dispersion and less time for local equilibration. Very low flow velocities may attain local equilibrium but with dispersion greatly overriding sorption effects. This is apparent from the column transport equation of Bastian and Lapidus (1956). Flow velocities chosen here (0.001 to 0.01 cm/sec) were in the range for sedimentary aquifer material given in Todd (1976). Practical column methods of isotherm measurement require that dispersion not be too great and that local equilibrium be attained. The amount of dispersion can be estimated from the observed breakthrough curves, while proof of local sorption equilibrium is difficult. If there were no other difficulties with column measurements, this proof could be obtained from demonstrated identity of isotherms measured by the batch and column methods. Invariance of the sorption isotherms calculated by the column methods with flow velocity is a necessary but not sufficient for local equilibrium. The "correctness" of column dynamic isotherms can only be verified by comparison with batch isotherm values, and literature indicates

column and batch methods may not agree exactly (e.g., Bilkert and Rao, 1985).

Flow velocities were too slow to use the frontal analysis by characteristic point (FACP) method (Jacobson et al, 1984) for isotherm measurement. Breakthrough curves from the present study indicated considerable dispersion, and the FACP method does not contain a means of correcting calculated isotherms for dispersion. An empirical FACP correction has been proposed by Zverev et al (1974), but has not yet been supported by mathematical analysis of the column transport process. There may be considerable departure from local equilibrium at high flows, but this could not be checked because calculated sorption coefficients by the frontal analysis method were found independent of flow rate below that producing column retainer blockage. Blockage was indicated by a sudden rise of back pressure from less than 100 psi to the column structural safety limit (2700 psi) specified by the manufacturer.

Measurement porosity and system dead volume.

Frontal analysis requires measurement of the column and system dead volume which is the sum of the column void volume and the volume of tubing, photometric cells, column ends and fittings. The latter are known, so the task of measurement of dead volume becomes that of determining the column void volume, which is also used in calculation of porosity. The obvious method is to weigh the dry packed column empty and again full of solvent. Weight difference and the solvent density give the void volume from which one can calculate porosity. Difficulties arise if the solvent phase is compressible and applied pressure is above atmospheric. A completely dry packing cannot be obtained without subjecting clay minerals

12

and organic substances to temperatures where they are irreversibly altered. Packing density may vary after solvent is passed and pressure is cycled several times. Irregular and multisized particles rearrange and sort. Aquifer materials used here were air dried for 24 hours at $60^{o}C$, and columns were dry filled with vertically tapping as suggested by Snyder and Kirkland (1979). Determination of the column void volume is a topic of active research. Some of the problems are reflected by the work of McCormick and Karger (1980) and Knox and Kalizan (1985). The frontal analysis method adds a constraint on dead volume determination. Column void volume by the weighing method should agree exactly with that calculated from the column flow rate and the observed breakthrough curve of an unretained solute.

A mechanical problem with column packing becomes apparent when one tries to assure that there is no dead space between the packing retainers and the packing, or that the packing bulk density is homogeneously distributed in the column space. Techniques in practical liquid chromatography have been developed to deal with this. Commercial units can compress plastic LC columns after they are packed. Some columns have movable end pieces that can be adjusted to conform to and slightly compress the packing bed. Neither method is applicable here because organic polymers must be used in their construction. A satisfactory solution to this problem has not yet been found using acceptable construction materials, i.e. stainless steel and glass.

Selection of an unretained solute for frontal analysis.

Several substances have been considered as unretained solutes for groundwater contaminant transport research: Br^- or Cl^- ionic salts with

alkali and alkaline earth cations; benzoic acid in anion form, ^3H_2O (tritiated water); ^2H_2O (deuterated water), Freon 12 and Freon 23. Betson et al (1985) describe the use of several of these tracers in column and field studies of groundwater transport. The halides, Br^- and Cl^- are most often used on the assumption that small anionic species will not be retained by the negative charges on aquifer material surfaces at normal pH. Data given in Nkedi-Kizza et al (1983) for soil column breakthrough of pulses containing ^3H_2O, $^{45}Ca^{++}$ and $^{36}Cl^-$ labels in $CaCl_2$ solutions indicated that Ca^{++} ions are more retained than $^{36}Cl^-$ or ^3H_2O, which are themselves nearly similarly retained. Thus, refractive index measurement is not a perfect breakthrough indication for halide salt solutions because the cation is retained, probably in a complex ion exchange reaction with H^+ and other cations on the aquifer material. Chloride analysis of the column effluent gives a better approximation to an unretained solute. The ideal non-retained solute should not interact with sorbent surfaces. ^3H_3O protons will exchange with Si-OH protons and organic functional group protons, and may thus be retained. The chemistry of the aquifer material sorbent is altered by the presence of a dissolved salt in a complex and unknown way, so halide salts or other ions are not ideal unretained substances. Justification for the use of Cl^- here is based on the above-noted conclusion of similarity to ^3H_2O transport. Nkedi-Kizza et al (1982) have shown that $^{36}Cl^-$ is very slightly retained relative to tritiated water on soils at low flow rates, but this difference was neglected here. Tritiated water could not be used at the time due to license limitations. Deuterated water is probably suitable, but expensive to analyze. The noble gases and freons require expensive analysis and special sample handling methods to avoid volatility losses.

Proof of non-retention must await greater knowledge of the sorbent surface and its chemical interactions with these solutes. Nkedi-Kizza et al (1982) allude to this problem in their consideration of pH interdependence with salt ion sorption for $CaCl_2$, but of course cannot explain behavior in this terribly complex situation.

Imposition of a step increase in unretained solute concentration must alter the surface of the sorbate in ways which are now undeterminable. There is no ideal unretained reference solute. If the solute chosen is not perfectly unretained, dead volume calculated will be too high and the sorption coefficients measured by frontal analysis will be underestimated. It appears that ^3H_2O is the best available "unretained" substance for aquifer material, but this is not confirmable at present.

Column design requirements.

The requirements of columns to be used with aquifer material packings are stringent:

a. Dead space at column ends must be negligible relative to packing void volume.

b. Column packing retainer must retain all particles of packing, but not block flow.

c. Column and system materials must not sorb solutes to be investigated.

d. Columns must be free from corrosion by salt solution in the presence of some oxygen, as corrosion products of metals are good sorbents.

e. Columns must withstand applied pressure to at least 100-200 psi.

f. Wall and end effects must be minimized by column design.

Requirements c, d, and e apply to chromatographic system tubing,

connections, and measurement cells. The all stainless steel system used here does not meet requirements b and d. An ideal system meeting these requirements for solute listed would be all heavy borosilicate glass, with sufficiently fine glass frit packing retainers, glass connections, and glass capillary tubing. It should have no plastic seals or organic lubricants. No such chromatographic system is commercially available, but designs are being developed at this laboratory. It is, however, relatively simple to design an all-glass ampoule system for performing batch equilibration sorption measurements on systems of aqueous solutions and aquifer materials.

Consideration of Relative Simplicity for Column and Batch Isotherms.

Batch isotherms require constant temperature and measurement of liquid and solid phase concentrations and amounts. Column isotherms require constant temperature and flow rate, along with measurement of packing porosity and of two solute breakthrough concentrations as functions of time. Column isotherm measurement is more complex and this implies more potential sources of error in sorption coefficients. It is not satisfying to use complex methods and costly equipment to obtain data that can be collected more simply. Accordingly, batch techniques appear preferable to column techniques for sorption measurement. A batch system is better definable than a dynamic flowing column system because knowledge of hydrodynamics of the former system is not necessary for batch system thermodynamic description.

Competitive sorption.

Competitive sorption was considered in multiple sorbate column experiments done with 1 methylnaphthalene-1,2 dichlorobenzene solutions, but

as for single sorbates, one point K values were obtained due to column measurement time limitations. The time required for one complete isotherm with seven points by frontal analysis is about thirty days under the conditions used. Complete batch isotherms on these materials can be done much more rapidly (in about two days) and were done on each of the aquifer materials with 1,2 dichlorobenzene and with 1 methylnaphthalene, and on Carswell aquifer material with 1 methylnaphthalene-1,2 dichlorobenzene mixtures. All batch isotherms were linear at concentrations used in the column experiments, so linear sorption coefficients are presented.

Competitive sorption is defined by Helfferich and Klein (1970) as an interference resulting from competition of the different sorbate molecules in solution for the limited capacity (or number of sites) on the sorbent. Addition of different molecules to the mobile phase of fixed composition in another solute will reduce its solvent phase concentration due to competition. Competitive sorption is the basis for displacement chromatography, and Jacobson et al (1987) have presented an excellent work on measurement of competitive adsorption isotherms by frontal chromatography that is relevant to groundwater transport of contaminants. Competitive sorption of components of a sorbate mixture can be identified by changes in the isotherm of a given component caused by the presence of other sorbates. Jacobson et al. (1987) showed competitive sorption of phenol and p-cresol from water on octadecylsilica, but this competitive sorption did not occur below 5 milimole/liter. At the low concentrations presented in Table 2, isotherms for mixtures did not show competition and were linear as noted above.

Competitive sorption had not been demonstrated in literature for ground water contaminant transport, and was not detected by batch or column

17

experiments done here. Absence of competition is explained by the low organic solute concentrations in contaminated groundwater and by the predominance of non-specific interactions (e.g., van der Waals forces, etc.) in uptake of non-polar sorbates by aquifer materials. If the column experiment results of Jacobson et al (1987) are applied to groundwater aquifer material situations by assuming octadecylsilica "similar" to an aquifer material, it appears that non-linearity and sorbate competition do not occur below phenol concentrations of about 400 mg/liter. This is higher than the water solubility of any sorbate in this program, and a factor of ten higher than the water solubility of complete JP-4 fuel (see for example, Smith et al 1981). Competitive sorption may occur in the vicinity of environmental releases of mixtures of large amounts of highly water soluble polar organic compounds, but apparently does not occur for liquid hydrocarbon fuels or chlorinated solvents.

Results of column sorption of ODCB and 1CH₃N on Aquifer Materials.

Conditions and results of frontal chromatography of ODCB and $1CH_3N$ solutions on aquifer materials are presented in Table 2. Sorption coefficients for the same systems from batch equilibrations are presented here (from Stauffer, MacIntyre, and Wickman 1989) for comparison with the column derived sorption coefficients. Trends observed in batch sorption coefficients were followed by the column sorption coefficients, but the column coefficients were always lower than batch coefficients. Means and standard deviations of the ratio (K from V_1)/K $_{batch}$ for each sorbate averaged over all sorbents are:

ODCB, $\bar{x}$ = 0.49 and σ = $\pm$0.17

$1CH_3N$, x = 0.45 and σ = $\pm$0.12.

This implies an empirical relation such as:

$$K_{column} = K_{batch} \times 0.47$$

This discrepancy between methods is probably not experimental error. Bilkert and Rao (1985) observed a similar factor between column and batch sorption coefficients for nematicides on soils. They noted that this may be a consequence of failure to reach local equilibrium in the column. Two step kinetics have been observed in batch approach to equilibrium data, and it may be that the second slower step is not completed during the contact period in columns. In this case the observed K might be a function of linear flow rate, but linear flow velocities used here were varied by a factor of ten from 0.01 cm/sec to 0.001 cm/sec without apparent effect on K.

Table 2. Sorption Chromatography Results on Aquifer Materials (from Stauffer, MacIntyre, and Wickman 1989).

Sorbent	Q	d	Sorbate	C	W	ϵ	ρ_b	ρ_s
Carswell	3	6.2	ODCB	1/4	13.48	0.361	1.78	2.79
"	6	6.2	$1CH_3N$	1/4	13.48	0.361	1.78	2.79
"	3	6.2	$1CH_3N$	1/4	13.48	0.361	1.78	2.79
"	1.5	6.2	ODCB	1/4	13.48	0.361	1.78	2.79
"	1.5	6.2	$1CH_3N$	1/4	13.48	0.361	1.78	2.79
"	5	21.2	$1CH_3N$	1/4	153.24	0.368	1.74	2.79
"	5	21.2	$1CH_3N$	1/4	153.24	0.368	1.74	2.79
"	5	21.2	$1CH_3N$	1/4	153.24	0.368	1.74	2.79
"	5	21.2	$1CH_3N$	1/4	153.24	0.368	1.74	2.79
Tinker	3	6.2	$1CH_3N$	1/4	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/8	13.72	0.345	1.81	2.77
"	3	6.2	ODCB	1/2	13.72	0.345	1.81	2.77
"	3	6.2	ODCB	1/2	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/4	13.72	0.345	1.81	2.77
"	3	6.2	ODCB	1/2	13.72	0.345	1.81	2.77
"	3	6.2	ODCB	1/8	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/4	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/16	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/8	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/2	3.72	0.345	1.81	2.77
"	3	6.2	ODCB	1/2	13.72	0.345	1.81	2.77
"	3	6.2	ODCB	1/4	13.72	0.345	1.81	2.77
"	3	6.2	$1CH_3N$	1/2	13.72	0.345	1.81	2.77
Borden	1.5	6.2	$1CH_3N$	1/2	13.68	0.326	1.81	2.67
"	1.5	6.2	$1CH_3N$	1/4	13.68	0.326	1.81	2.67
"	1.5	6.2	$1CH_3N$	1/8	13.68	0.326	1.81	2.67
Lula	0.75	4.6	$1CH_3N$	1/2	7.42	0.336	1.79	2.69
"	0.75	4.6	$1CH_3N$	1/2	7.42	0.336	1.79	2.69
Blytheville	5	21.2	$1CH_3N$	1/4	152.50	0.340	1.73	2.62
"	5	21.2	ODCB	1/2	152.50	0.340	1.73	2.62
"	5	21.2	$1CH_3N$	1/4	152.50	0.340	1.73	2.62
"	5	21.2	ODCB	1/8	152.50	0.340	1.73	2.62
Barksdale	10	21.2	$1CH_3N$	1/3	157.75	0.351	1.79	2.75
"	10	21.2	ODCB	1/4	157.75	0.351	1.79	2.75
	10	21.2	ODCB	1/3	157.75	0.351	1.79	2.75

Q is column flow rate (ml/h)
d is column diameter (m)
C is sorbate concentration as fraction of saturation concentration
W is packing weight (g)
ϵ is packing porosity
ρ_b is bulk density
ρ_s is packing material density

20

Table 2 (continued)

Sorbent	V_2	V_1	V_1'	k from V_1'	k from V_1	k Batch	Detection for V_1'
Carswell	3.91	2.81	3.01	0.07	0.08	0.18	RI
"	4.66	2.81	3.28	0.25	0.29	0.45	RI
"	6.06	2.81	2.93	0.23	0.24	0.45	RI
"	3.99	2.81	3.10	0.07	0.09	0.18	RI
"	7.17	2.81	3.05	0.31	0.32	0.45	RI
"	59.8	32.5	42.0	0.12	0.18	0.45	$[Cl^-]$
"	68.3	32.5	37.1	0.20	0.23	0.45	RI
"	67.1	32.5	32.0	0.23	0.23	0.45	$[Cl^-]$
"	73.5	32.5	32.0	0.27	0.27	0.45	$[Cl^-]$
Tinker	5.18	3.00	3.02	0.16	0.16	0.44	RI
"	5.18	3.00	3.02	0.16	0.16	0.44	RI
"	3.81	3.00	3.04	0.06	0.06	0.10	RI
"	3.88	3.00	3.31	0.04	0.04	0.10	RI
"	4.48	3.00	3.09	0.10	0.11	0.44	RI
"	3.79	3.00	3.07	0.05	0.06	0.10	RI
"	3.75	3.00	3.03	0.05	0.05	0.10	RI
"	5.19	3.00	3.06	0.16	0.16	0.44	RI
"	5.42	3.00	2.99	0.18	0.18	0.44	RI
"	5.20	3.00	2.93	0.17	0.16	0.44	RI
"	4.57	3.00	2.93	0.12	0.11	0.44	RI
"	3.31	3.00	2.93	0.03	0.02	0.10	RI
"	3.75	3.00	3.07	0.05	0.05	0.10	RI
"	5.92	3.00	3.47	0.18	0.21	0.44	RI
Borden	5.75	2.46	2.90	0.21	0.24	0.65	RI
"	5.95	2.46	2.91	0.22	0.26	0.65	RI
"	6.05	2.46	2.79	0.24	0.26	0.65	RI
Lula	3.12	1.39	1.73	0.19	0.23	0.51	RI
"	2.80	1.39	1.46	0.18	0.19	0.51	RI
Blytheville	182.8	29.0	28.75	1.00	1.01	3.06	$[Cl^-]$
"	82.8	29.0	30.00	0.35	0.35	1.28	$[Cl^-]$
"	295.0	30.0	--	--	1.74	3.06	--
"	110.5	30.0	--	--	0.53	1.28	--
Barksdale	128.46	31.0	36.37	0.58	0.62	0.96	$[Cl^-]$
"	66.96	31.0	39.26	0.18	0.23	0.30	$[Cl^-]$
	69.57	31.0	40.25	0.18	0.24	0.30	$[Cl^-]$

V_2 is retention volume of sorbate (ml)
V_1 is column dead volume (ml) from weight data
V_1' is column dead volume (ml) from unretained substance breakthrough curve
k is calculated sorption coefficient (liters/kg) assuming linear isotherm
RI indicates refractive index measurement
$[Cl^-]$ indicates chloride titration

Rao and Jessup (1983) speculated upon possible reasons that sorption equilibrium is not reached in columns at low flow rates that should yield sufficient contact time. They considered several models involving liquid filled pore dead space, diffusion through organic coatings on sorbent, and multiple kinds of sorption sites. No conclusions were reached, and the present work does not resolve the matter. It is also possible that the severe turbulence and energetic collisions between sorbent particles in a batch isotherm measurement may abrade particles and create new surface area and sites for rapid equilibration, perhaps to a different state than exists in columns. The author has earlier noted several difficulties with liquid column chromatography measurement of sorption coefficients; some of these can lead to apparently low K with respect to batch K (e.g., particle loss, packing channeling). Rao and Jessup (1983) state that further research on the disagreement between batch and column sorption is needed, and the present author concurs.

The observation of a general factor of about 0.5 almost independent of particular soil, aquifer natural or sorbate is tantalizing. An explanation might be obtained from a set of concurrent batch and column sorption measurements of selected slightly polar organic compounds on uniform particle size synthetic sorbents of somewhat known composition. Questions to be answered include:

1) Does the factor hold for an inorganic sorbate, such as geothite or kaolinite?

2) Does the factor hold for a C_{18} bonded phase spherical pellicular packing sorbate?

3) Do functional group substitutions on C_{18} by $-CN$, $-NH_2$ etc in the bonded phase affect the factor?

4) Does the factor hold both for pellicular and microporous bonded phase particles?

5) Is the factor dependent on the sorbent particle size in any of the above experiments?

The failure of column K data to agree with batch K data precludes the initially proposed thermodynamic analysis of column data using aquifer materials. There are no apparent advantages to column measurement of soil and aquifer material sorption, and it is recommended that batch isotherm data be used for comparison of aquifer sorption purposes, at least until differences between batch and column methods are understood. Kinetic investigations of sorption by column methods have been proposed by Rao and Jessup (1983). but seem fraught with complexity and do not permit unique interpretations of results. Kinetic measurements yield unique sorption mechanisms only when intermediates are observed microscopically or spectroscopically. The author believes kinetics of sorption in systems studied must be inerpreted empirically, and that there is now no best model for sorption kinetics measurement. Instead there are different, but mathematically similar methods using approximate and incomplete models of the sorption process.

Table 3 presents arithmetic average sorption coefficients for each aquifer material by both batch and column methods. ODCB was not run on Borden and Lula materials. The order of uptake by sorbents is similar within experimental error for the two methods.

Table 3. Sorption coefficients for 1CH$_3$N and ODCB on aquifer materials by column and batch techniques.

| | COLUMN | | BATCH | |
	1CH$_3$N	ODCB	1CH$_3$N	ODCB
Tinker	0.18	0.05	0.44	0.10
Carswell	0.25	0.08	0.45	0.18
Blytheville	1.38	0.44	3.06	1.28
Borden	0.26	--	0.65	0.30
Lula	0.21	--	0.51	0.14
Barksdale	0.62	0.23	0.96	0.30

It can be argued that, if reality and correctness of the factor near 0.5 is accepted, there is good agreement between the sorption coefficients for the aquifer material which were determined by independent analytical methods. However, application of this factor without understanding is not satisfying.

Work with sorbate binary mixtures was limited due to the need for GC analysis of many fractions from each column run. Mixture studies were further restricted when discrepancies were noted between batch and column methods, and time was allocated to establishing the magnitude of this difference. The last ODCB and 1CH$_3$N sorption coefficients on Blytheville material given in Table 2 were measured on an ODCB - 1CH$_3$N mixture such that column influent water was 1/4 saturated with 1CH$_3$N and 1/8 saturated with ODCB. The sorption coefficients obtained were slightly higher than those obtained in single solute uptake measurements, but there was insufficient data on Blytheville material to establish statistically significant differences.

Breakthrough curves for JP-4 solution on aquifer material.

The purpose of these experiments was to demonstrate the chromatography of JP-4 components under emulated aquifer conditions. JP-4 was equilibrated with water in the volume ratio of 1:100 to produce a saturated solution. This aqueous solution was diluted by an equal volume of water and loaded into a syringe pump. Chromatography was done under conditions similar to those used for simple hydrocarbon solutions; flow rates 5 ml/h, column 25 cm x 21.2 mm ID, packing with Blytheville aquifer material, dead volume calculation from Cl^- breakthrough curve when $CaCl_2$ concentration was stepped from 0.01 to 0.015M. Breakthrough of components of the solution was measured by collecting fractions over a 2-hour period in septum capped bottles kept at 0°C in an ice bath, extracting the content with 1 ml hexane containing tri-isopropyl benzene internal standard, and injecting the extract into a gas chromatograph with capillary column to analyze each component.

The breakthrough curves were generated from discrete points. Graphical integration was done on manually smoothed data, and the results checked by numerical integration in which areas were calculated for trapezoids corresponding to each data point.

Establishment of breakthrough curves for JP-4 components by this method was only possible for those components that are quite soluble in water and abundant in the JP-4. High molecular weight compounds (i.e., highly substituted benzenes and naphthalenes) and aliphatic hydrocarbons did not meet these conditions. Good breakthrough data was obtained for toluene, ethylbenzene, and the xylenes. The m and p xylenes were not separated by the gas chromatographic method used, so their sum was recorded, and used with the assumption that the two isomers also behaved similarly in liquid

chromatography on the aquifer material. This is supported by the
breakthrough curves are shown in Fig. 5. All concentrations are normalized
to those in the feed solution. Calculated K values were:

	K	Boiling Point ($^\circ$C)
toluene	0.30	110.6
ethylbenzene	0.39	136.2
m+p xylene	0.43	m 139.1, p 138.1
o-xylene	0.46	144.4

The K values increase with boiling point and with frontal elution time in
the same order as peaks for the compounds appeared in GC analysis of
extracts of fractions containing all five solutes. This trend is expected
but cannot be explained in terms of a sorption mechanism on the aquifer
material. Identities of the compounds were confirmed by GC-MS of the
extracts. Sorption coefficients observed here are in reasonable accord with
those measured for ODCB and $1CH_3N$, 0.53 and 1.74 respectively, on
Blytheville material under the same conditions. Results in Fig. 6 show
chromatography which might be anticipated for a JP-4 release to groundwater.
This situation has not yet been demonstrated here in field studies. Patrick
et al (1986) have injected water solutions of simple aromatic hydrocarbon
mixtures in tests at the Borden site, but have not yet injected liquid
hydrocarbon mixtures or petroleum products. Chromatographic separation must
occur for complex mixtures, as demonstrated here in laboratory emulation,
but sampling and analyses are much more difficult than with simple mixtures.
Burris and MacIntyre (1986) investigated solution of complex hydrocarbon

mixtures in water and noted that the approximate concentration of component compound C_i in water is given by $C_i = X_i C_i^O$, where X_i is the mole fraction of i in the hydrocarbon mixture and C_i^O is the solubility of the pure hydrocarbon. Each component i of a fuel mixture is present at low X_i, and C_O^i will be small for aliphatic or high molecular weight aromatic compounds, so C_i to be measured is small. This means that large ground water sample volumes must be taken in the field and that laboratory column chromatographic emulations of field situations require large sample volumes which are limited by the practical size of chromatographic columns. The author estimates that one liter samples should be taken for field release studies similar to the Borden work using jet fuels, and that these samples will require analysis using both solvent extractions and purge and trap isolation, followed by GCMS and GC-FID. Analysis of high molecular weight fuel components in groundwater has been ignored in most reported field studies and site investigations.

Emulation and Field Study of Nonlinear Sorption in Contaminant Transport by Groundwater.

Groundwater contaminant transport models that are applied include sorption by material in the saturated zone, and are currently based on the assumption of a linear adsorption isotherm. Sorption is then expressed in transport equations by a retardation factor, for example as presented in the compilation by Van Genuchten (1982). Contaminant distributions predicted from these equations will be in error when sorption isotherms are nonlinear, and other factors such as biodegradation and vaporization may be invoked to explain the apparent differences between model prediction and field observation. Nonionic organic compounds may have nonlinear isotherms on

27

soils and aquifer materials, and some examples are shown in Mingelgrin and Gerstl (1983). Transport equations with linear retardation factors have been used as approximations because inclusion of nonlinear isotherms produces equations more difficult to solve analytically. A general analytic solution of the transport equation for any nonlinear isotherm has not yet been obtained, but considerable progress has recently been made with analytic solutions in one dimension for parabolic and Langmuir isotherms.

This discussion applies some results from nonlinear chromatography to groundwater contaminant transport and proposes field tests to investigate the importance of isotherm nonlinearity in determining contaminant distributions in aquifers. Field studies of nonlinear sorption processes at sites similar to the current Borden site are suggested, because aquifer material in situ chemical environment, fluid dynamics and sedimentology cannot be duplicated in the laboratory. Sposito et al (1986) noted the need for field experiment tests of contaminant transport models in their discussion of stochastic transport models. In the following, some recent results from nonlinear adsorption chromatography literature are presented and their relevancy to groundwater contaminant transport calculations is considered. A field site research program that involves introduction of organic compounds having linear and nonlinear isotherms on the aquifer material is proposed. This will demonstrate the extent to which contaminant sorption isotherm nonlinearity produces contaminant distributions and transport velocities of transport that differ from predictions assuming linear sorption.

Recent chromatographic research on nonlinear sorption liquid chromatography has treated advective-dispersive transport with sorption for different classes of isotherms. Jaulmes et al (1986) treated the case of

second-order polynomial isotherms that can closely approximate Langmuir and some other observed isotherms. Arinshtein (1983. 1986) has given analytic solutions for advective-dispersive transport with a Langmuir isotherm, generalizing initial and boundary conditions in the latter paper. Zolotarev (1985) has given solutions for advective-dispersive transport with S-shaped isotherms for step function inputs (frontal chromatography). This area of research is active and more solutions for other isotherms and initial and boundary condition are anticipated (C. Horvath, personal communication). The present effort to relate this fundamental work on sorption chromatography to groundwater contaminant transport selects the formulations of Jaulmes et al (1986) for further consideration, because of the general utility of isotherm fitting by polynomials, and because this work is formulated for liquid chromatography. Liquid chromatography terms are the same as, or directly translate to those used in the groundwater literature. When a pulse (square wave) input is applied to a finite length column, the expression:

$$c_A^L (t,\zeta) = \frac{2}{\lambda U} \left(\frac{D'}{\pi t} \right)^{1/2} \exp \left(-\frac{\zeta^2}{4D't} \right) \Big/ \coth \left(\frac{\mu}{2} \right) + \mathrm{erf} \left(\frac{\lambda}{2(D't)^{1/2}} \right)$$

gives the concentration of the sorbate at the outlet as a function of time.

Where U = limit band progation velocity for zero sample size

t = time

$\zeta = Z - Ut$, Z = length along column

c_A^L = concentration of sorbate in liquid phase

$\mu = \dfrac{aU^2 \lambda}{2D'}$

29

a = peak area parameter

$$\lambda = \frac{(k_0'' - 2k_0' \, W_A^{01}}{(1 + k_0')}$$

and k_0' and k_0'' are constants of the parabolic isotherm

W_A^{01} = partial molar volume of sorbate at zero concentration

D = dispersion coefficient

$D' = D/(1 + k_0')$

All these parameters can, in principle, be measured independently and used to define the output peak. Jaulmes et al did not do this, but used experimentally determined peak shape and retention times to determine a, μ, λ, and D. This fitting procedure is conceptually similar to that used in calibratives groundwater transport models.

Some features . this solution are relevant to groundwater situations. Peaks are symmetrical for linear sorption isotherms. For nonlinear convex (Langmuir-Type) isotherms, peak fronts are sharp and tails diffuse. The converse holds for concave isotherms. The center of sorbate mass of a peak with linear sorption isotherm is independent of sorbate concentration, but is retarded for a convex isotherm and advanced for a concave isotherm. Groundwater contaminant plume shape and the velocity of center of contaminant mass thus depends upon the sorption isotherm for the contaminant on the aquifer material.

If we consider a pulse injection as has been described at the Borden site by Mackay et al (1986), plan views of instantaneous sorbate concentration like their Figure 8 will be nearly elliptical for sorbates with linear isotherms. If isotherms are nonlinear and convex, a common

situation, the sorbate distributions for similar groundwater conditions will become tear-drop shaped with the elongated portion of the distribution directed back up the hydraulic gradient. The frontal boundary of the tear drop will be very sharp with the sharpness limited by dispersion. The center of mass will arrive at a given distance from the source more quickly than would have been the case if the isotherm were linear.

Jaulmes et al (1986) state this as:

$$t_m \simeq t_R / 1 + \frac{D' t_R}{L^2} - \lambda C_m$$

where C_m = maximum peak concentration

t_R = limit of retention time for zero sample size

t_m = retention time corresponding to maximum peak concentration

L = column length

λ and D' have been given above

or as a linear approximation when λCm and $\dfrac{D' t_R}{L^2}$ are small with respect to unity:

$$\frac{t_m}{t_R} \simeq 1 - \frac{Dt_R}{(1 + k_0')L^2} + \lambda C_m$$

If the isotherm is convex, k_0', the first derivative of the isotherm slope must be less than one so $(1 + k_0')$ must be positive. $|\lambda| C_m \ll 1$ for

not too high concentrations, so t_m is less than one. That is, $t_m < t_R$. These assumptions can be confirmed from the data tabulated by the authors.

The approximate solution for the convex polynomial isotherm case demonstrated by Jaulmes et al is similar to the exact solution for a Langmuir isotherm by Arinshtein (1983).

The theory of nonlinear liquid chromatography is not completely worked out, but is sufficiently developed for use in groundwater contaminant transport calculations. Its use in transport models requires determination of isotherms over the concentration range occurring in an aquifer. If the isotherms are not exactly linear, the transport equation with a constant retardation factor cannot validly be used.

A site at Columbus, Mississippi, is presently under consideration. The research proposed here is similar in concept to the recent program of Mackay et al (1986) on light chlorinated hydrocarbons and their more recent work on benzene-toluene-xylene mixtures (Patrick et al 1986). These organic solutes all had linear sorption isotherms on the aquifer material. It is proposed that similar releases of two component mixtures of organic compounds be made, with one of the components linearly sorbed and the other nonlinearly sorbed. The components must be selected such that they do not degrade appreciably during the experiment. Sampling wells and procedures should be similar to those now in use with the Borden mixture studies.

The linearly sorbed compound should be an aromatic hydrocarbon such as ethylbenzene, i-propylbenzene or 1-methylnaphthalene. Several candidate compounds have been found to give nonlinear isotherms on soils. Selection among those that may give Freundlich or Langmuir type isotherms on aquifer materials will involve consideration of a number of polar nonionic pesticides, herbicides and industrial chemicals. The choice is based on

32

extent of departure from linearity of the sorption isotherm and on

resistance to biodegradation. Both requirements must be met on the site

aquifer material. A high concentration of the sorbate will be used to

assure that effects of nonlinearity of sorption on contaminant transport are

observable. $C_6H_6Cl_6$ (hexachlorocyclohexane) is a candidate compound with

isomers that Mingelgrin and Gerstel (1983) have reported to sorb

nonlinearly, and that is somewhat resistant to biodegradation. The optimum

nonlinearly sorbed compound will be selected from results of a laboratory

program in which batch sorption isotherms and biodegradability of a number

of slightly soluble organic compounds will be determined using the site

aquifer material. Experiments will be conducted on columns packed with site

aquifer material, using the sorbates selected above. The results will

indicate chromatographic processes that should occur in field tests.

The objective is to examine the proposition that nonlinear sorption

behavior of a contaminant solute in groundwater causes its transport rate

and concentration distribution to differ appreciably from that of a similar

solute exhibiting a linear isotherm. If the proposition is supported by the

proposed field work, contaminant transport model calculation should be based

on a mass balance equation similar to that given by Jaulmes et al (1986)

namely,

$$\frac{\partial C_A^L}{\partial t} = \frac{U_0}{1 + k_0'} \left(1 - C_A^L \left(\frac{k_0'' - 2k_0' W_A^{0'}}{1 + k_0'}\right)\right) \frac{\partial C_A^L}{\partial Z} = \frac{D}{1 + k_0'} \frac{\partial^2 C_A^L}{\partial Z^2}$$

where U_0 is the velocity of the aquifer flow. All other terms in this

equation have been defined above. One notes the differences between this

equation and a similar expression for a linear isotherm given for example in Bear 1979 (using the term definitions above) as

$$\frac{\partial C_A^L}{\partial t} + \frac{U_0}{1 + k} \frac{\partial C_A^L}{\partial Z} = \frac{D}{1 + k} \frac{\partial^2 C_A^L}{\partial Z^2}$$

where k is the linear sorption coefficient times $\varepsilon/\rho b$. The differences are an expression of isotherm nonlinearity. If isotherms are measured carefully to obtain good k_0' and k_0'' values, the Jaulmes et al (1986) equation can be solved numerically for groundwater transport situations for given initial and boundary conditions. The field work proposed will provide data needed to demonstrate solutions in an unconfined aquifer.

The site at Columbus, Mississippi, is presently instrumented and operated by The Tennessee Valley Authority. Initial visits indicate its suitability of the site and the potential to begin field work in FY 1989. If administrative actions are successful, collection of aquifer material for laboratory work will be done in FY 89. A central theme of this work is to consider transport of organics in solution, alone and in mixtures, as a two or three dimensional chromatography problem. Since there is relatively little vertical transport observed in most groundwater test site studies, there is a strong analogy between transport from a ruptured fuel tank or a dump site and the transport and separation of chemicals on a thin layer chromatography plate (Helling 1971). The chromatographic literature may be of considerable use in improving understanding of groundwater contaminant transport.

Some recent numerical models have been presented for groundwater contaminant transport with non-linear sorption, and the SUTRA model of Voss

34

(1984) has been selected for initial use in this research. SUTRA is a two dimensional finite element model with vertical averaging and is suited for contaminant transport evaluation in the saturated zone using data from the proposed field test program.

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